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(19) Japanese Patent Office

Unexamined Patent Gazette

(11) Unexamined Patent Application (Kokai): 48–79896
(43) Date of Publication: October 26, 1973
(21) Japanese Patent Application: 47-10111
(22) Application Date: January 27, 1972
Request for examination: Not yet submitted
Total of 5 pages [in original]

Internal Office Registration Nos.	(52) Japanese Classification
6779 45	26 (5) D 12
6911 45	26 (5) D 101, 21
7195 45	26 (5) D 101, 11
7365 48	25 (1) D 32

(Revenue stamp: ¥3000)

Patent Application (1)

January 27, 1947

Commissioner of the Patent Office: Mr. Takehisa Ido

1. Title of the Invention

Method for Producing Polyester

2. Inventor

Address: 1-13 Honkatata-cho, Otsu-shi, Shiga-ken
Name: Toshiyuki Mizumoto (and one other)

3. Applicant

ZIP Code: 530
Address: 8, Dojimahama-dori 2 chome, Kita-ku, Osaka-shi
Name: (316) Toyobo Co., Ltd.
Representative: Kunio Kawasaki

4. Attachments

(1) Specification 1 copy
~~(2) Drawings 1 copy~~
(3) Copy of application 1 copy

SPECIFICATION

1. Title of the Invention

Method for Producing Polyester

2. Claims

A method for producing polyester wherein bis-(β-hydroxyethyl)terephthalate or a mixture of bis-(β-hydroxyethyl)terephthalate and at least one other bifunctional compound is polycondensed in the presence of a titanium compound catalyst to produce a polyester with a high degree of polymerization so that at least 85% of the repeating structural units of the polyester are ethylene terephthalate units, characterized in that a phosphorus compound is added to the molten polyester once the polycondensation reaction has been completed[1].

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention is characterized in that when bis-(β^2-hydroxyethyl)terephthalate or a mixture of bis-(β^3-hydroxyethyl)terephthalate and at least one other bifunctional compound[4] is polycondensed in the presence of a titanium compound catalyst to produce a polyester with a high degree of polymerization so that at least 85% of the repeating structural units of the polyester are ethylene terephthalate units, a phosphorus compound is added to the molten polyester once the polycondensation reaction has been completed. This object has the effect of improving the color tone of the resulting polyester.

A catalyst is used when polyester is produced so that polycondensation will proceed smoothly and the polyester will be obtained in an economically efficient manner. However, it is known that the polycondensation speed and the quality of the polymer, such as the color tone of the resulting polyester, depend to a great extent on the catalyst that is used.

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[1] See Amendment 1, page 575 of the original; Item 5(1) of Amendment (2) of the original Japanese text.
[2] See Item 5(2) of Amendment (2) of the original Japanese text.
[3] See Item 5(3) of Amendment (2) of the original Japanese text.
[4] See Amendment 1, line 1 of the table on page 547 of the original Japanese text.

Many compounds are known as effective polycondensation catalysts for the production of polyester, and it is common knowledge that of these, titanium compounds such as tetraalkyl titanates, titanyl oxalates, titanyl oxalic acid, and titanium tetrachloride can be used as polycondensation catalysts.

Although these catalysts have very strong catalytic activity when compared to other metals[5], the resulting polyester is discolored and the catalysts cannot be regarded as suitable for polycondensing polyesters used as the starting materials for fibers or films. When a very small amount of a titanium compound is added as the catalyst in such a case, the color tone of the resulting polyester is good, but such an amount has little catalytic effect and the object of the reaction cannot be easily realized[6].

On the other hand, conventional methods are known whereby a phosphorus compound is added to the polyester as the coloration-inhibiting agent, either before polycondensation or once polycondensation is 30 to 60% complete (JP (Kokoku) 33-3748), but when a phosphorus compound is present during polycondensation, certain polycondensation catalysts lose their activity and polycondensation does not proceed smoothly.

In particular, the above-mentioned titanium compounds are rendered completely inactive by phosphorus compounds and cannot be present together with phosphorus compounds during polycondensation.

The inventors performed intense research in order to ameliorate the disadvantages of titanium compounds that have high activity as polycondensation catalysts for the production of polyesters but cause extreme discoloration, and, as a result, it became clear that the discoloration associated with the titanium compounds is eliminated when these compounds are deactivated with a phosphorus compound. Focusing[7] on the fact that the activity of a polymerization catalyst becomes unnecessary once a specific limiting viscosity is reached, the inventors successfully prevented discoloration from being caused by a titanium catalyst, and greatly improved the color

[5] Refer to Item 5(4) of Amendment 2 of original Japanese text.
[6] Refer to Item 5(5) of Amendment 2 of original Japanese text.
[7] Refer to Item 5(6) of Amendment 2 of original Japanese text.

tone of the resulting polymer by means of adding a phosphorus compound to the molten polyester once a specific degree of polymerization had been reached.

The method of the present invention has considerable industrial significance in the sense that it makes it possible to add a titanium compound catalyst in a greater amount, to reduce the polycondensation reaction time, and to obtain a polyester with a good color tone.

The method of the present invention will now be discussed in detail.

The bis-(β[8]-hydroxyethyl)terephthalate that is used in the present invention can be produced either by means of the esterification of dimethyl terephthalate and ethylene glycol, or by means of the direct esterification of terephthalic acid and ethylene glycol or ethylene oxide, and polycondensation is performed after adding a bifunctional compound[9] to this product as needed.

Examples of this bifunctional compound[10] include dicarboxylic acids such as terephthalic acid, isophthalic acid, adipic acid, sebacic acid, and 2,6-naphthalene-dicarboxylic acid; glycols such as propylene glycol, 1.4[11]-butanediol, pentaerythritol, polyethylene glycol, and cyclohexane dimethanol; and aromatic oxy acids such as para-[12]oxybenzoic acid. Pigments such as titanium oxide and carbon black can also be added.

The polycondensation reaction is divided into a first step leading up to the production of a polyester with a specific limiting viscosity, and a second step consisting of adding and uniformly mixing the phosphorus compound with the resulting polyester.

The first step consists of heating under normal pressure and polycondensation under reduced pressure. The appropriate degree of mixing[13] during heating under normal pressure is 240 to 270°C, and the appropriate heating temperature during polycondensation under reduced pressure is 270 to 290°C.

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[8] See Item 5(3) of Amendment 2 of the original Japanese text.
[9] See Amendment 1, line 2 of the table on page 574 of the original Japanese text.
[10] See Amendment 1, line 3 of the table on page 574 of the original Japanese text.
[11] See Item 5(7) of Amendment 2 of the original Japanese text.
[12] See Item 5(8) of Amendment 2 of the original Japanese text.
[13] See Amendment 1, line 4 of the table on page 574 of the original Japanese text.

The heating time under normal temperature varies with the type and amount of other bifunctional compounds[14] when those are added, as well as with the temperature, agitation method, and the like, but is within a range of 10 to 150 minutes.

The amount in which the titanium compound catalyst is added is 0.0005 to 0.02 mol%, and preferably 0.001 to 0.01 mol%, in terms of the acid component. The compound can be added at any time leading up to the polycondensation reaction. For instance, the titanium compound can be added after the beginning stages of esterification or ester exchange, or it can be added before the heating of the first step under normal pressure, or between the heating under normal pressure and the polycondensation under reduced pressure. The addition method can be either direct addition or addition after dissolution in a solvent such as water or ethylene glycol.

Examples of titanium compounds include tetraalkyl titanate, titanyl oxalates, titanyl oxalic acid, and titanium tetrachloride. Specific examples include tetraethyl titanate, tetra(iso-propyl)[15], partial hydrolysis products thereof, titanyl ammonium oxalate, titanyl sodium oxalate, titanyl potassium oxalate, titanyl calcium oxalate, titanyl strontium oxalate, sodium chloro-titanate, and ammonium fluorotitanate.

The polycondensation time under reduced pressure varies with the amount in which the titanium compound catalyst is added, as well as with the temperature, degree of reduced pressure, agitation method, and the like, but conditions are preferably selected such that this time is within a range of 20 to 120 minutes.

As long as the phosphorus compound is a liquid at room temperature, it can be added without pre-treatment, or it can be added after being dissolved in a solvent such as toluene, xylene, or diphenyl ether during the second step. This step consists of adding the phosphorus compound to the molten polyester obtained as described above, and uniformly mixing the ingredients. The addition method can be an addition[16] performed in a state of reduced pressure after the valves of the evacuation system have been closed, or an addition performed after the system has been returned to normal pressure. Agitation is continued for 1 to 30 minutes, and

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[14] See Amendment 1, line 5 of the table on page 574 of the original Japanese text.
[15] See Item 5(9) of Amendment 2 of the original Japanese text.
[16] See Item 5(10) of Amendment 2 of the original Japanese text.

preferably 5 to 10 minutes, after the addition in order to uniformly mix the phosphorus compound. Moreover, in the case of continuous polymerization, the phosphorus compound can be added[17] at the outlet from the polymerization vessel, or the compound can be added to the polyester with the help of using a line mixer or the like once the polyester exits the polymerization vessel.

The appropriate amount in which the phosphorus compound is added is 1 to 50 equivalents, and preferably 5 to 20 equivalents, per titanium atom of the titanium catalyst compound used.

Examples of phosphorus compounds include hypophosphorous acid, phosphorous acid, phosphoric acid, and alkyl esters or aryl esters thereof. Specific examples include trimethyl phosphite, triethyl phosphite, triphenyl phosphite, trimethyl phosphate, triethyl phosphate, triphenyl phosphate, diethylphenyl[18] phosphonate, and the like. A method for preparing a condensation product of phosphorus oxychloride and bisphenol A can be given as an example of the production method thereof[19].

The method of the present invention will now be described in specific terms with the aid of working examples. The term "parts" in the working examples refers to parts by weight. The limiting viscosity [η] is the value measured at 30°C in a mixed solvent (phenol/tetrachloroethane = 60/40), and the polymer color tone is the b-value on the Hunter scale.

(Working Examples)

Working Example 1

First, 267 parts of bis-(β^{20}-hydroxyethyl)tetraphthalate and 75 parts of terephthalic acid were introduced into an autoclave for polycondensation with an agitator and distillation tube attached, and heated for 30 minutes at 260°C under normal pressure in a nitrogen current. Then titanyl potassium oxalate dissolved in ethylene glycol was added at 0.003 mol% in terms of acid component, the system was gradually brought to a reduced pressure, and initial condensation was performed for 30 minutes at 20 mmHg. The degree of pressure reduction was raised and

[17] See Item 5(11) of Amendment 2 of the original Japanese text.
[18] See Item 5(12) of Amendment 2 of the original Japanese text.
[19] See Item 5(13) of Amendment 2 of the original Japanese text.

polycondensation was performed for 60 minutes at 275°C under 0.1 mmHg. Then the valve of the distillation tube was closed and the agitator was stopped. The system was kept in a state of reduced pressure as trimethyl phosphate (pre-dissolved in 10 parts of xylene) was added at 0.02 mol% in terms of the acid component. Agitation was restarted and the polymer was released five minutes later from the outlet at the base of the vessel into a water bath and recovered in the form of chips.

The limiting viscosity [η] of this polymer was 0.64, and the b-value (color tone) was 4.1.

Comparative Example 1

Polycondensation was performed as described in Working Example 1 without adding the trimethyl phosphate. The limiting viscosity [η] of the resulting polymer was 0.65 and the b-value (color tone) was 7.1.

Comparative Example 2

The trimethyl phosphate in Working Example 1 was added at the same time as the titanyl potassium oxalate, and polycondensation was performed for 150 minutes. The limiting viscosity [η] of the resulting polymer was 0.28 and the b-value (color tone) was 3.0

Working Examples 2 through 9 and Comparative Examples 3 and 4

Polycondensation was performed by means of the same method as described in Working Example 1, with the exception of the conditions indicated in Table 1. The limiting viscosity [η] and the b-value (color tone) of the resulting polymer were as shown in the table.

[20] See item 5(3) of Amendment 2 of the original Japanese text.

Table 1

	Titanium compound catalyst	Amount added mol%	Phosphorus compound	Amount added mol%	Average time (minutes)	[η]	b-value
Working Example 2	Potassium titanyl oxalate	0.003	Phosphorous acid	0.02	60	0.63	1.2
Working Example 3	Potassium titanyl oxalate	0.003	Triethyl phosphite	0.05	60	0.64	3.6
Working Example 4	Potassium titanyl oxalate	0.003	Triphenyl phosphite	0.03	40	0.62	4.3
Working Example 5	Potassium titanyl oxalate	0.003	Diethylphenyl phosphonate[21]	0.06	30	0.43	3.6
Working Example 6	Tetraethyl titanate	0.005	Phosphoric acid	0.06	45	0.62	4.7
Working Example 7	Tetraethyl titanate	0.005	Trimethyl phosphate	0.05	45	0.64	5.0
Working Example 8	Tetraethyl titanate	0.005	Triethyl phosphite	0.10	45	0.63	4.0
Working Example 9	Tetraethyl titanate	0.005	Triphenyl phosphite	0.06	70	1.03	7.2
Comparative Example 3	Tetraethyl titanate	0.005	-	-	45	0.64	8.7
Comparative Example 4	Tetraethyl titanate	0.0005	-	-	150	0.58	(illegible).3

Applicant: Toyobo Co., Ltd.

5. Other Inventors

Address: 1300-1, Honkatata-cho, Otsu-shi, Shiga-ken

Name: Tetsuo Wakai

[21] See Item 5(14) of Amendment 2 of the original Japanese text.

Procedural Correction (Voluntary)

Date: July 1, 1972

Commissioner of the Patent Office: Mr. Takehisa Ido

1. **Case No.**
   1972 Patent Application No. 10111
2. **Title of the Invention**
   Method of Producing Polyester
3. **Party Making the Amendment**
   Relation to the Case: Applicant
   8, Dojimahama-dori 2 chome, Kita-ku, Osaka-shi
   (316) Toyobo Co., Ltd.
   Representative: Kunio Kawasaki
4. **Sections Amended**
   "Claims" and "Detailed Description of the Invention" of Specification
5. **Amendment Details**
   (1) The Claims are amended as on the separate page.
   (2) The Specification is amended as shown below.

Translation page number	Line	Incorrect	Correct
2	14	Bifunctional compound	Multifunctional compound
4	10	Bifunctional compound	Multifunctional compound
4	11	Bifunctional compound	Multifunctional compound
4	20	Degree of mixing	Temperature
5	2	Bifunctional compound	Multifunctional compound

2. Claims

A method for producing polyester wherein a mixture of bis-(β-hydroxyethyl)-terephthalate or bis-(β-hydroxyethyl)terephthalate and at least one other multifunctional compound is polycondensed in the presence of a titanium compound catalyst to produce a polyester with a high degree of polymerization so that at least 85% of the repeating structural units of the polyester are ethylene terephthalate units, characterized in that a phosphorus compound is added to the molten polyester once the polycondensation reaction has been completed.

Amendment in accordance with Clause 17 of the Patent Law

1972 patent application No. 10111 (JP (Kokai 48-79896, October 26, 1973, Unexamined Patent Gazette No. 48-799) has been amended in accordance with Clause 2 of the Patent Law and is therefore entered as follows.

Internal Office Registration Nos.	(52) Japanese Classification
6779 45	26 (5) D 12
6911 45	26 (5) D 101, 21
7195 45	26 (5) D 101, 11
7365 48	25 (1) D 32

Published August 26, 1975

Procedural Correction (Voluntary)

(In accordance with Provision 1-2 of Clause 17 of the Patent Law)

Date: April 24, 1975

Commissioner of the Patent Office: Mr. Hideo Saito

1. **Case No.**

   1972 Patent Application 10111

2. **Title of the Invention**

   Method for Producing Polyester

3. **Party Making the Amendment**

   Relation to the Case: Applicant

   8, Dojimahama-dori 2 chome, Kita-ku, Osaka-shi

   (316) Toyobo Co., Ltd.

   Representative: Kazuji Otani

4. **Sections Amended**

   "Claims" and "Detailed Description of the Invention" of Specification

5. **Amendment Details**

   (1) The Claims on page 2 of the translation are amended as on the separate page.

   (2) The "-(β" on line 13 of page 2 of the translation is amended to "-(2."

   (3) The "-(β" on line 14 of page 2, line 7 of page 4, and line 20 of page 6 of the translation is amended to "-(2."

   (4) The word "compound" is inserted after "metal" on line 6 of page 3 of the translation.

   (5) The phrase "...but such an amount has little catalytic effect and the object of the reaction cannot be easily realized" on lines 9 and 10 of page 3 of the translation is amended to "but catalytic activity is low and is therefore a serious problem."

   (6) The word "intently" is inserted after "Focusing" on line 23 of page 3 of the translation.

   (7) The "1.4" on line 13 of page 4 of the translation is amended to "1,4."

   (8) The "para-" on line 14 of page 4 of the translation is amended to "para."

   (9) "Titanate" is inserted next to "isopropyl" on line 13 of page 5 of the translation.

   (10) The phrase "to the molten polyester" is inserted after "addition" on line 24 of page 5 of the translation.

   (11) The phrase "to the molten polyester" is inserted after "added" on line 3 of page 6 of the translation.

   (12) The "diethylphenyl" on line 11 of page 6 of the translation is amended to "diethylbenzene."

(13) The phrase "... and the like. A method for preparing a condensation product of phosphorus oxychloride and bisphenol A can be given as an example of the production method thereof" on lines 11 to 13 of page 6 of the translation is amended to "... and polyphosphonates such as condensation products of phosphorus oxychloride and bisphenol A."

(14) The phrase "diethylphenyl phosphonate" under "Phosphorus compound" in the line for Working Example 5 in Table 1 on page 8 of the translation is amended to "diethylbenzene phosphonate."

Attachments

(1) Request for Examination of Application 1 copy

[Separate page]

2. Claims

A method for producing polyester wherein bis(2-hydroxyethyl)terephthalate or a mixture of bis(2-hydroxyethyl)terephthalate and at least one other bifunctional compound is polycondensed in the presence of a titanium compound catalyst to produce a polyester with a high degree of polymerization wherein at least 85% of the repeating structural units of the polyester are ethylene terephthalate units, characterized in that a phosphorus compound is added to the molten polyester once the polycondensation reaction has been completed.